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Battelle Technical Review

IN THIS ISSUE:

Science And The Graphic Arts

This visual guide aids the Titanium Metallurgical Laboratory, located at Battelle, to keep abreast of all current and past research on titanium sponsored by the U. S. Government. Kept up to date by the TML staff, the guide is available to Armed Forces and government civilian agencies interested in titanium research. Its purpose is to help them in planning and coordinating their research programs. TML also maintains an information center whose facilities are open to all government contractors and their suppliers, who are interested in titanium. Gathered there are more than 18,000 extracts of all available literature on the subject, including reports on governmental and private research.

CHECKPOINT FOR TITANIUM RESEARCH

Volume 5, Number 10
October 1956

BATTELLE TECHNICAL REVIEW

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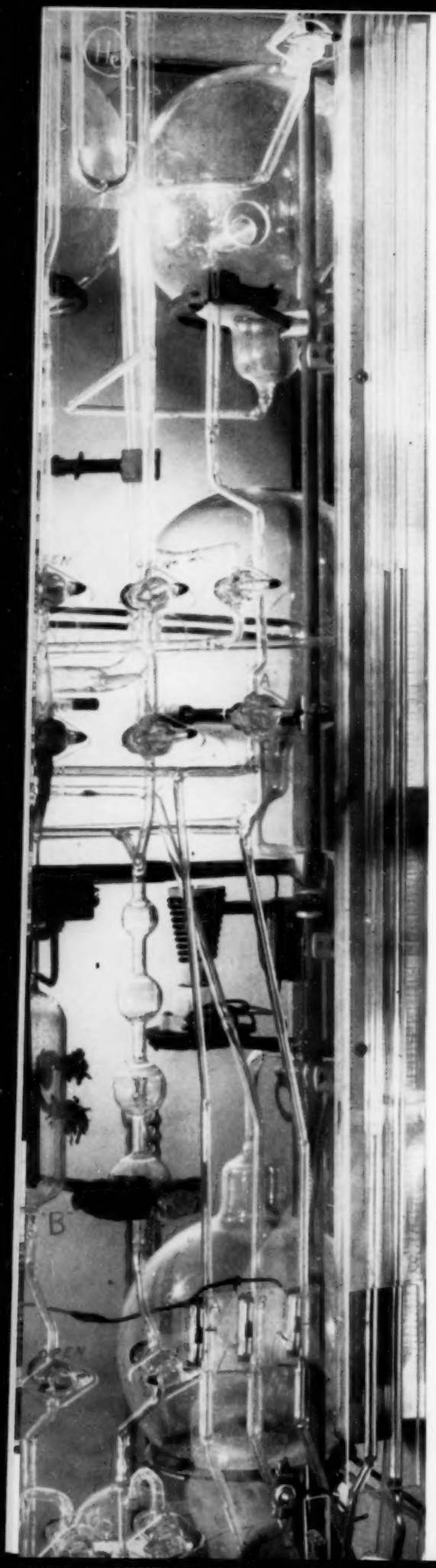

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Abstracts of articles and papers in a wide variety of technological fields from more than 1350 journals published throughout the world. Abstract selection largely reflects the primary areas of Battelle research.

Adsorption apparatus used to determine surface area, porosity, and adsorption characteristics of solids.

Getting Answers to Problems

"BUT MY BUSINESS IS DIFFERENT . . ."

This plaint is being heard less and less by laboratories that conduct contract research for industrial firms. As research becomes more widespread, businessmen are becoming increasingly aware of the fact that the same basic scientific principles apply to all businesses—and that research management and methodology are the things that really count in getting answers to problems. This understanding, in turn, is causing more firms to turn to research, and is adding impetus to technological progress.

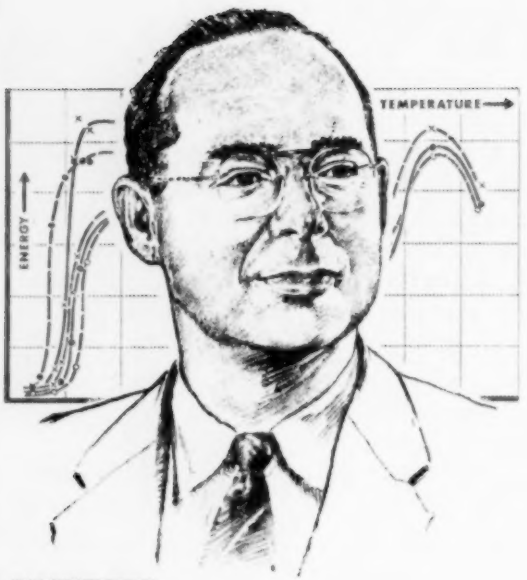
Getting answers to industrial or commercial problems does not, as businessmen are finding, require a separate, highly developed technology for the particular field. Neither does the research laboratory need to be staffed with people who had long technical experience in the specific industry. But to get answers most readily, an adequacy of specialists in the basic sciences and an organization proved in its ability to solve problems are required. A well managed research laboratory with a highly diversified and competent staff and a good record of prior accomplishment is usually a better bet for solving problems than any length of experience in a particular field. Many of the toughest problems of business and industry have been cracked—not by those seasoned in the business or industry itself—but by laboratory scientists who were capable of applying universal scientific principles and methods to them.

A large proportion of business and industry is related only obscurely to one or more of the basic sciences. A department store, for instance, would seem to have little in common with mathematics or physics—yet many of the present problems of large-scale merchandising can be attacked by mathematical analysis and by the application of electronic and mechanical devices to operations. No degree of experience in merchandising would ever lead to the creation of electronic and mechanical equipment to handle department store inventory and billing procedures. Likewise, a lumber company is only obscurely related to chemistry, yet chemistry made plywood possible.

The most research-wise managements no longer look upon their businesses as offspring of any one science, art, or trade, to be catered to only by that science, art, or trade. They invite all aid possible in solving their problems—going to laboratories that can provide it. They know that getting the answer is what counts. And they leave the details to those who make getting the answer their profession.

Clyde Williams

President and Director,
Battelle Memorial Institute



VIGNETTE

RESEARCH CORRELATOR

DR. WILLIAM J. HARRIS, JR.

The growing demands upon American research facilities and manpower call for increasing efficiency in their utilization. Dr. William J. Harris, Jr. of Battelle believes that the best way to accomplish this is for private industry and government to reflect a common awareness of current problems and current research activities.

Bill's experience and present responsibilities at Battelle enable him to play a significant role in correlating the research efforts of industry and government. As Assistant to the Institute's Director, he is responsible for liaison between Battelle and sponsors, both industrial and governmental. Since his association with Battelle, one of his primary interests has been the establishment of the Titanium Metallurgical Laboratory. TML is designed to aid government agencies and industries concerned with the use and production of titanium by providing them with a central source of information and with advisory and other services.

Prior to joining Battelle, he was Executive Secretary of the Minerals and Metals Advisory Board of the National Research Council and the National Academy of Science. In this capacity, he helped plan the Board's organization and scope. After receiving his Sc.D. in metallurgy from the Massachusetts Institute of Technology, Bill served as head of the Ferrous Alloys Branch of the Naval Research Laboratory. Earlier he was on active duty as head of the Aircraft Armor Branch of the Bureau of Aeronautics. During his service with the Bureau, aluminum armor for aircraft and nylon body armor were introduced.

He is chairman of two project advisory committees of NRC's Ship Steel Committee and chairman of the Materials Advisory Board Panel on the Titanium Sheet Rolling Program.

He is active in the American Institute of Mining, Metallurgical, and Petroleum Engineers, especially the Institute of Metals Division. Currently vice chairman of IMD and a member of its executive committee, he has been nominated as senior vice chairman for the coming year. He has also served as chairman of the AIME national membership committee.

His research studies in ferrous physical metallurgy and on armor and ship steels have led to more than a dozen publications. For one of these he was co-recipient of AIME's Matthewson Medal for the best publication in the Society's *Annals* in 1950.

At home, Bill and his wife enjoy their young daughter and son. What time remains is taken up by the Accokeek Citizens Association, the Moyane Company, the Alice Ferguson Foundation, and other community activities. Fishing and hunting come out a poor last.

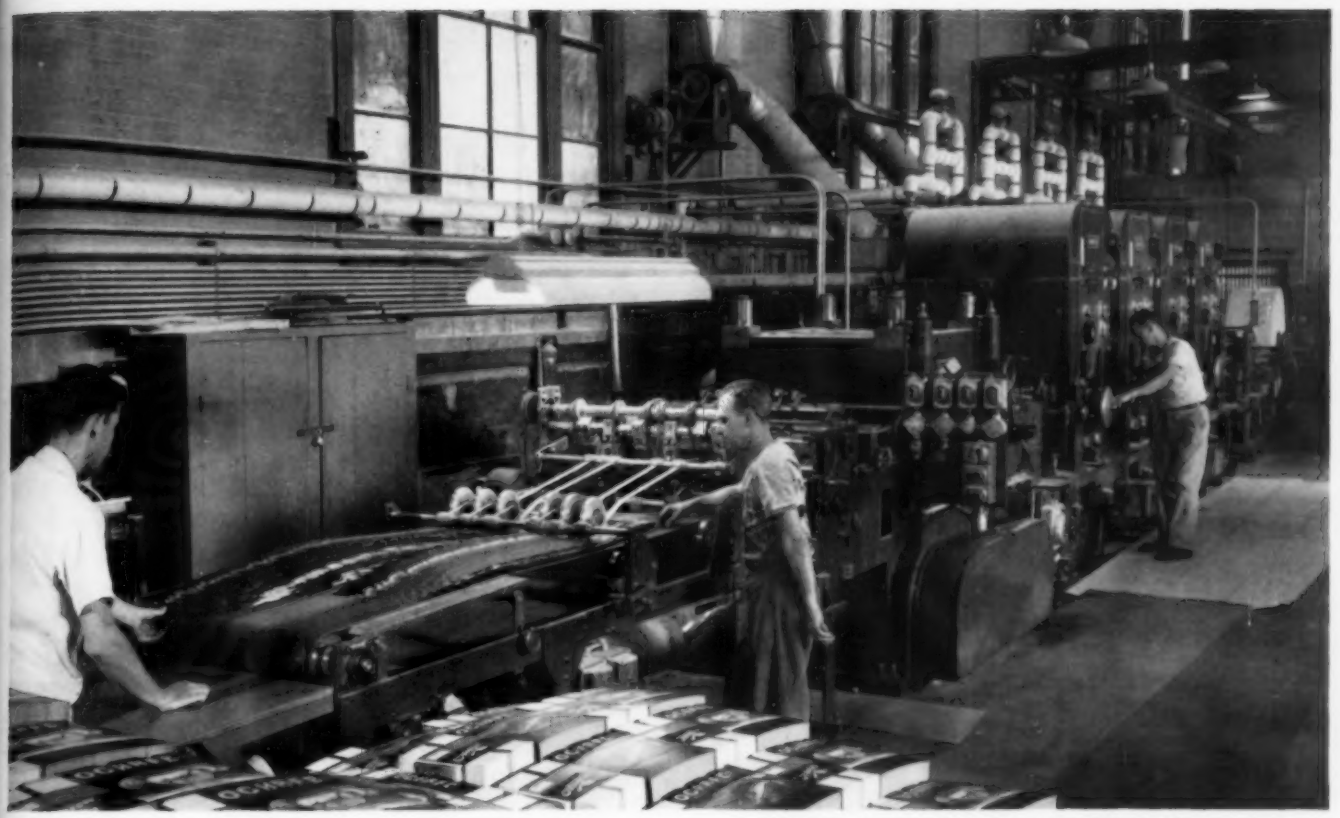


Photo Courtesy of Gaylord Container Corporation

An over-all view of in-line rotogravure equipment. Kraft stock feeds from a roll through four rotogravure units, a cutter, a creaser, and a stripper—all automatically operated. With this multiple-unit machine, one million cartons, printed in four colors, are produced in a five-day, two-shift operation.

Science and the Graphic Arts

Though the graphic arts were largely developed by craftsmen, future advances may be expected to come primarily from research in a variety of scientific fields.

by EDWIN E. GRAVES

THE GRAPHIC ARTS ORIGINATED over 20,000 years ago when Old Stone Age men made paintings on the walls of caves to depict their pursuit of the animals on which their lives depended. Later, in Mesopotamia, writing first developed as attested by the finding of large quantities of records inscribed on clay tablets. Once the art of writing was well established, it became an accepted method of communication. With the development of parchment and paper, the dissemination of news by means of hand-written leaflets and the collecting of manuscripts in libraries became general.

First in ancient Greece and Rome and then in medieval Europe the production of books was accomplished by copying manuscripts. Naturally, books were costly and limited in number, and the communication of ideas was highly restricted. This is certainly one of the reasons why the people of the ancient and medieval worlds failed to develop experimental science and why many of the learned men had difficulty in spreading the knowledge of their discoveries.

Today, scientists are not so limited in the communication of their ideas and discoveries. On the contrary, so much published information is available that scientists find it difficult to keep up with all the current development, even in their own field of specialization. For this happy situation, we have the

true artists and craftsmen of the printing profession to thank. As a result of their ingenuity and skill, movable type was invented and developed, and printing presses were devised and improved. Through the centuries, each new generation of craftsmen has added to the art and efficiency of the printing process, and they are still contributing to the improvement of the graphic arts.

With the advent of the industrial revolution, though engineers applied first steam, and then other forms of motive power to the presses, the basic method of printing remained the same. However, in recent decades, science has played an increasingly important role in the development of new graphic arts techniques.

Graphic arts is not a science in itself but is a composite of nearly all the physical sciences. Chemistry contributes to improved papers, inks, methods of etching printing plates, and materials such as rubber and plastics for printing plates. Physics is concerned with such problems as how ink can be best transferred to paper and how static electricity can be eliminated. Metallurgy is important to improved printing plates and presses. Electrical engineering and electronics play an important role in providing improved means for registering multicolor images precisely and in handling large volumes of paper at high speeds. Ceramics contributes by providing dimensionally stable mounting materials for photoengravings. More detailed examples of the dependency of the graphic arts on many of the sciences will be seen from the research examples given below.

Beginnings of Technical Research

One of the earliest research studies in the printing field was made in 1912 by Dr. William Blum at the Bureau of Standards in cooperation with the International Association of Electrotypers. Dr. Blum's studies of copper sulfate electrotyping solutions were published in 1914. The reaction was so favorable that in 1916, the International Association of Electrotypers placed a research project at the Bureau. World War I brought the investigation to a halt before a good start was possible, but the work was resumed in 1924 and continued to 1932. At that time, the Electrotypers placed a project at Fenn College in Cleveland which lasted until 1934. In 1935, a survey study, followed by a research investigation, was placed at Battelle Memorial Institute. This work was completed in 1938, and was resumed in 1941 at Battelle for Printing Plates Research, Inc.

In 1943, the above research had resulted in one of the most outstanding developments in the history of electrotyping, the invention of a plastic electrotype mold. Prior to this, electrotypers had of necessity been forced to tolerate the nuisances of powdered graphite and molding-wax compounds. The graphite was used to effect separation in wax molding and again subsequently to apply an electrically conductive film on the wax mold to permit electrodeposition of the shell in making duplicate printing plates. The graphite permeated the clothing of workers, made the floors slick, and generally contaminated nearly everything in the plant. The fumes from the molten wax were always present. In addition, the wax would stick between type and was difficult to remove from the face of the finished electrotype.

By 1940, an efficient procedure had been developed for applying a film of silver to a wax or other type of surface. Thus, graphite could be replaced by silver for use as the conductive film. However, graphite still had to be used as the separating medium in making the wax mold.

Printing Plates Research, Inc., a group of electrotypers formed to conduct research investigations on improving electrotype manufacture, placed a project at Battelle in 1941. The assigned problem was to improve the methods used in backing up the electrotype sheets with metal. During some unavoidable delays in obtaining materials and equipment for this study, Institute technologists took the opportunity to explore the possibilities of molding in a thin plastic sheet instead of in wax or lead. The first results were so promising that this became the major investigation instead of the casting problem. Further experiment showed that vinyl was an excellent molding medium and experimentation resulted in developing methods for using it in place of wax as the mold material. By use of a film of silver on it to make it conductive for electroplating, the use of graphite was completely

The author has participated in both research and administrative activities at Battelle. He has aided in the investigation of bearings and lubricants and in reactor fabrication problems. Graves has also been engaged in licensing activities in connection with Battelle-held patents. More recently he has held administrative and project advisory responsibilities in the Institute's graphic arts diviison. In this connection he has carried on patent liaison activities relating to xerography developments. A graduate of The Ohio State University, Graves is an active member of the Technical Association of the Graphic Arts.

eliminated. Today, the plastic mold is used by an overwhelming majority of electrotype foundries.

The above is but one example of the dividends of applying science to the graphic arts. Another phase of graphic arts which early recognzied the possible contributions of science was the lithographic industry. The lithographers organized the Lithographic Technical Foundation in 1924 and initiated research at the University of Cincinnati in 1925. In 1945, their laboratories were moved to their present location at the Glessner House in Chicago. Currently they are spending about $250,000 per year on research to improve lithographic methods and materials. A large measure of the phenomenal growth of the lithographic industry since 1925 is due to the splendid research results produced by the Lithographic Technical Foundation.

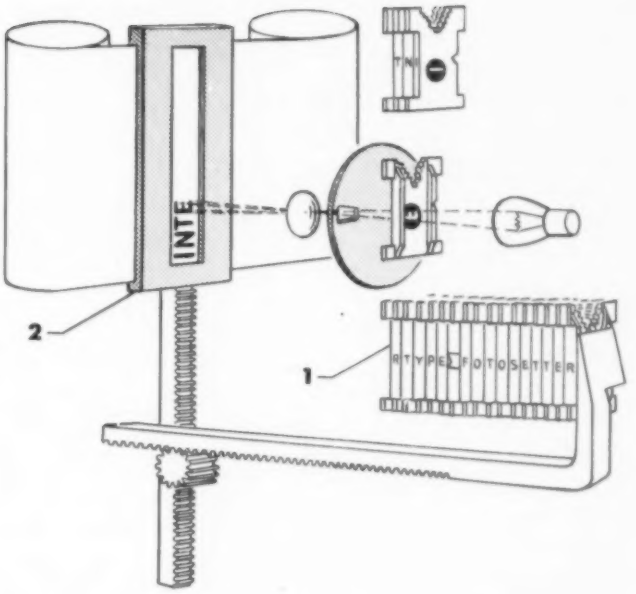
The nonprinting aspects of the graphic arts were not forgotten in these earlier days of research. Both the paper and the bookbinding industries soon became aware of science as a means for improving their products.

The Institute of Paper Chemistry began operations in Appleton, Wisconsin, in 1929. It has maintained a continuous research program concerning problems in paper chemistry and paper manufacture. Also, in cooperation with Lawrence University, the Institute of Paper Chemistry has helped make available advanced training for college graduates interested in the pulp and paper industries.

The Employing Bookbinders of America, around 1930, employed a research associate to study some of the problems of book manufacture. This work was done in the Technical Division of the Government Printing Office and was continued until about 1944.

Undoubtedly there were other investigations prior to World War II, but the above were most widely publicized. After the war, the graphic arts industries could not help but note how the use of technically trained people and research had so effectively solved problems arising with the increased demands for production during the war. Simultaneously with the end of the war, demands for printing multiplied rapidly and progressive companies began to invest in scientific research to improve their methods, equipment, and materials to meet their greater production demands.

It would be impossible, of course, to describe all the research activities in progress in the graphic arts. The Research and Engineering Council of the Graphic Arts Industry, Inc., listed 382 specific investigations in progress in 1952. These covered the activities of well over 100 United States concerns or organizations. Undoubtedly many others were not reported for various reasons.



In this photo typesetter, as in the Linotype machine, matrix lines (1) are justified after being assembled. The individual matrices, which contain the letters in negative film form, are individually raised and photographed. The film carriage (2) drops the distance proper for the matrix each time a new matrix is fed into the camera mechanism.

These research investigations cover one or more facets of each of the following parts of the graphic arts industry: bindery operations and materials; color; composition; printing processes, including gravure, letterpress, lithography, silk screen, dry-relief offset, flexography, and engraving; plate making and materials; paper; ink; press design, engineering, and operation; photography; rollers for presses; xerography; and materials handling. Some of the significant scientific developments are described later. They illustrate the trend of thinking of the graphic arts industry as to the role that science and technology may play in improving the quality of its products. These examples also serve to show the sciences that are of importance to the graphic arts.

Xerography

Xerography, invented by Chester F. Carlson, is a completely new photographic process, requiring no chemicals or liquids, and utilizing a photosensitive plate that is unique in that it is not destroyed by exposure to light.

In its original state of development, xerography appeared to be a mere technical curiosity and, like many inventors, Carlson had difficulty in selling the process to industry. However, Battelle became aware of xerography and the Institute undertook studies of the process in its laboratories. By 1947, xerography had been developed sufficiently that The Haloid Com-

pany, Rochester, New York, saw potentialities for the process in the field of photocopying. The company has carried on developmental work on this and other uses of the process. Other industrial concerns and several government agencies, including the Signal Corps, the Engineer Corps, the Navy, and the Air Force, have also sponsored much research in the field.

The above research activities have resulted in a completely new business that now amounts to millions of dollars each year, and affords employment to hundreds of people. The process is used commercially for reproducing single and multiple copies of documents, letters, magazine articles, business forms, and similar items. It also is used to prepare offset lithographic plates, prepare spirit-duplicating masters, make enlarged copies of microfilmed subjects, and record oscilloscope images. Both manually operated and fully automatic machines are available.

Many sciences contribute to the development of xerography. The field of solid-state physics is involved in studies of improved photoconductive coatings used as the photosensitive element in the process. Organic chemistry plays an important part because photoconductive coatings can be made of powdered photoconductors mixed in an organic binder. Both classical physics and organic chemistry are important to research on powders used to develop the xerographic image; classical physics aids in understanding and controlling the electrostatic fields involved and the electrical properties of the powders; and organic chemistry plays a part in formulating new, improved powders having the proper electrical and physical properties. A knowledge of conventional graphic arts processes contributes greatly to investigations of methods of using xerography to prepare conventional printing plates. Metallurgy plays a role in selecting suitable conductive backing plates to support the photoconductor. Finally, mechanical and electrical engineering are indispensable in the design and development of new xerographic equipment.

Chemical Etching of Magnesium Printing Plates

Because of its light weight, high strength, and ease of processing, magnesium has been used for the past ten years to good advantage for many types of engraved printing plates. It had been evident for some time that a faster, more economical etching process would greatly expand the use of magnesium in the printing-plate industry.

The Dow Chemical Company, Midland, Michigan, set its chemists to work about seven years ago to investigate improved methods of etching magnesium. They did not, however, decide to concentrate their investigations on chemical etching until they had also evaluated the potentialities of electrolytic and mechanical methods. This is an excellent example of the role that the scientific approach plays in determining how best to tackle a problem and thus prevent waste of effort and money in unprofitable research efforts. In this case, Dow selected the chemical approach for the following reasons:

1. Magnesium dissolves rapidly in many common acids.
2. Little work had been done with magnesium printing plates from the chemical viewpoint.
3. A chemical rapid-etch process would parallel the popular chemical method used in conventional etching.
4. Chemical etching of magnesium would probably be as fast as electrical etching, and the problem of removing magnesium from an electrolyte would not exist.
5. Mechanical etching or vapor blasting was already receiving attention by another research laboratory.

Proceeding with its investigations, Dow spent about five years in developing a new chemical method for etching magnesium. The result is a process that will etch line engravings to a depth of about 0.020 inch in five minutes as compared with 60 minutes required by previous methods. In addition, the process produces engravings whose quality is equal to and often superior to that of conventionally etched plates. After its chemists developed this process, Dow's engineers contributed their technical knowledge to the design and construction of an etching machine that allows the process to be used under the closely controlled conditions that produce engravings of optimum quality.

Dow, in cooperation with the research laboratories of the American Newspaper Publishers Association, has modified the process for use in etching halftones as well as line work. Newspapers, particularly, are finding the process useful because of its speed and economy.

A Three-Color Printing Process

Conventional commercial color printing is done by printing a minimum of three colors, plus black, in halftone reproduction. The cost of camera work, plate making, color correction, and press time is so great that it must be spread over a great many reproductions to be economical.

Dr. C. E. K. Mees of Eastman Kodak set as an objective the development of a simplified, economical process whereby scientists and other authors could

obtain color illustrations for their books, periodical articles, and reports at a reasonable price. Working on the theory that it should be possible to obtain good color reproduction with only three basic colors, a new color-reproduction system was developed.

The development of this process, like other graphic arts processes, also employed the knowledge of many sciences. Application of the physics and chemistry of color made possible the elimination of all color corrections. Chemistry aided in the development of an improved printing plate which can be made more simply, is completely free of surface texture, has excellent ink-water differentiation, and allows the use of offset lithography as the printing method. Optics and photographic technology were employed to construct a special enlarger to make the necessary color separations directly from masked 35-mm color transparencies. By application of good engineering practices, registration of the color images on the offset press was made possible by mechanical means, thus decreasing the time necessary to set up the press for printing. Last, but not least, ink chemistry enabled development of new color inks that are more amenable to good three-color printing than process inks used in conventional color printing.

Phototypesetting

From the time of Gutenberg in the 15th century until recent years, type was set by hand, or in such mechanical typesetters as the Linotype machine. With the application of technical knowledge derived from the fields of electrical engineering and electronics, however, it is now possible to set type automatically.

The first commercially available phototypesetter, (see illustration), developed by Intertype Corporation, employs photography in the setting of type. One of the biggest potential uses of photographic typesetting is in composing display advertising for newspapers. By phototypesetting, it is possible to combine the type on film with screen photoprints of illustrations in accordance with the advertiser's layout. This provides a preliminary composite photoproof that can be submitted for approval. If changes are necessary, a section of film can be replaced where necessary, and only after the advertiser has approved the work does it become necessary to commit anything to metal.

Color Scanners

In printing color pictures, a separate plate must be used for each color printed. To make each plate, it is necessary that the color originals be separated into what are known as "color separations". Previously dependent largely upon the skill of a photographer, electronics is now being adapted widely for this purpose.

A color scanning machine was developed by Time, Inc. It is a lathe-like machine—that is, a shaft extends from end to end of the machine. Upon the right end is mounted a transparent drum. The color transparency to be copied is wrapped around this transparent drum. At the left part of the machine, four sheets of sensitized photographic film are wrapped—one each for yellow, red, blue, and black, in that order. A spot of light projected from a lamp scans the color transparency wrapped on the transparent drum at the right of the rotating shaft. The light spot beams a varying color pattern to photoelectric cells by mirror through three filters. These filters separate the color values and by means of other photoelectric cells, pass them on to the electronic amplifying circuits. In turn, the color values (varying currents) are sent to the four lamps which expose the four revolving sensitized negatives on the drum at the left side of the shaft.

In operation, the drums are advanced along the axis of the shaft, so that the four color separations are exactly in register with each other and with the original transparency. The action is similar in principle to a screw-cutting lathe. The scanning operation requires about one hour for an 8-inch by 10-inch color transparency at 250 lines to the inch.

In-Line Equipment

The graphic arts have taken advantage of the obvious benefits to be gained from production-line type of equipment made possible by research. A notable example is the use of in-line equipment by the packaging industry. Thus, in box making, a continuous pass of stock from a roll through a series of in-time units provides for printing, sheeting, creasing, die-cutting, stripping, embossing, bronzing, and folding.

In other presses, two printing processes are employed in line to print four colors in quick succession on a die-cut, stripped sheet. Two of the printing units employ the letterpress process, and two of them print from a rubber offset blanket. Printing from the rubber blanket permits good coverage over the die-cuts and creases.

Many more examples of the contributions of science to the graphic arts could be cited that are equally as significant as those noted here. In nearly all cases, it would be seen that no single science is more important than the others in the industry. In fact, it often requires the combined knowledge of all the fields of science and engineering to solve even a single problem.

What have all the contributions of science meant to the industry? The answer can probably be best stated in terms of the size of the graphic arts as compared with other industries. Although research has by no means been entirely responsible for the high position of the graphic arts among manufacturing industries, it certainly is responsible for a large part of it.

According to the *Statistical Abstract of the United States: 1955,* the printing, publishing, and allied industries, exclusive of the packaging field, ranked eighth among manufacturing industries in 1953 in terms of contribution to national income (net value added to product by manufacture). Their total was exceeded only by the following manufacturers, in the order stated: metals and metal products; machinery, except electrical; food and kindred products; electrical machinery; automobiles and automotive equipment; chemicals and allied products; and transportation equipment other than automotive. In numbers of firms engaged in manufacturing, the graphic arts industry ranks second, being exceeded only by the number of firms that manufacture food and kindred products. In 1952, there were 30,147 establishments in the printing, publishing, and allied trades. Of these, 29,683 had fewer than 250 employees. In total number of employees, the graphic arts ranked ninth in 1952 among manufacturers. In number of salaried employees, however, the graphic arts ranked fourth in the same year.

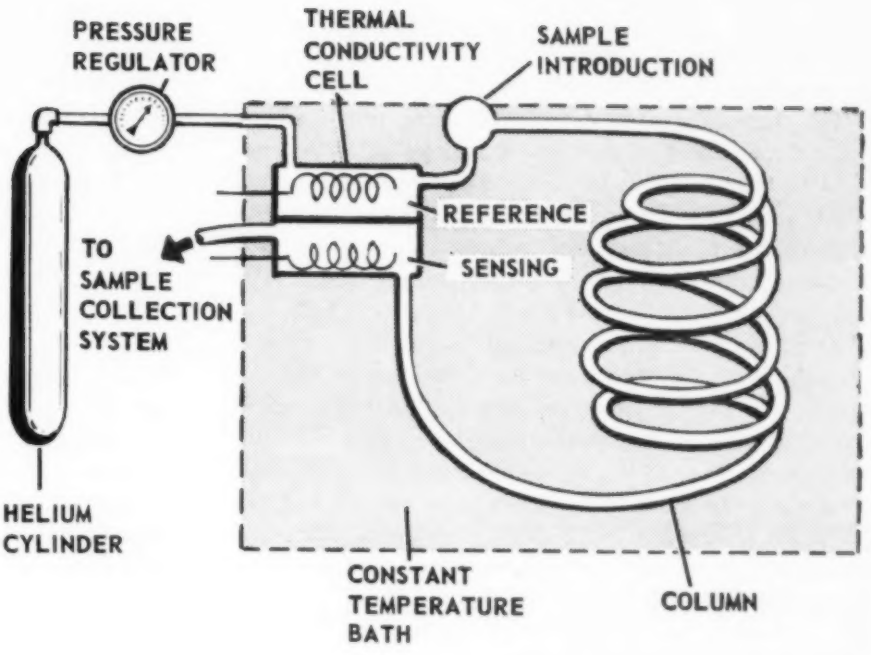
What is the future of science in the graphic arts? There is no doubt but that science will continue to play a still greater part in advancing the industry. This is signified by the increasing number of dollars being spent on research and development by the industry, and, more significantly, by the increasing number of firms spending these dollars for research.

However, there still is great need for tremendously increased research effort in the industry. This is dictated by the rapidly increasing demands of consumers of graphic arts products for improved quality of product at lower costs and for new products. In addition, the uses of graphic arts in unrelated industries is a growing field that demands greater attention. For example, photoengraving is finding widespread use in the making of printed electrical circuits and in making metal masks for color television tubes.

As in all industries, research costs money. However, as others have so aptly put it, research is comparable with marriage. If you carefully considered the financial angles before contracting a marriage, there would be no wedding. Yet, marriage is a popular institution, as evidenced by its wide acceptance among all civilized races. The benefits may not always be obvious, but in the long run, it pays outstanding dividends.

"For really efficient use of nuclear reactors we need even now materials which can operate in the range from 5,000 to 10,000 degrees Fahrenheit. The highest temperatures attained in current operating practice, specifically for turbine blades, is in the neighborhood of 1,650 degrees Fahrenheit. With the current scale of materials research effort, this figure has been rising steadily at about 100 degrees Fahrenheit per year for the last decade. Any abrupt advance in technology, providing increased operating temperatures of even 100 or 200 degrees, can mean the complete obsolescence of an engine type and therefore an entire air fleet."

Lawrence R. Hafstad
Vice President in Charge of Research
General Motors Corporation



1. *Schematic diagram of a gas chromatograph showing the essential elements of such an apparatus.*

Gas Chromatography

by CHARLES L. TEITELBAUM

Gas chromatography is only a few years old, yet it has already proved itself a highly useful tool for many purposes in chemical and allied fields.

IF A CHEMIST WERE ASKED TO name the greatest single advance in the last twenty years in the techniques of separating mixtures of chemical compounds, he would certainly have to answer that it was the development of chromatography. We must use the word "development" instead of "discovery" because, like so many scientific advances, chromatography was discovered long before its potentialities even began to be realized.

In 1903, the Russian botanist M. Tswett filled a glass tube with powdered chalk and poured a solution of plant pigments on top of the column. He then found that if he allowed pure solvent to flow through the column, a series of colored bands, separated by uncolored zones of chalk, moved down the column. By pushing the chalk out of the column and extracting each colored zone with solvent, he obtained purified plant pigments from what had been a complex mixture. Tswett called this new technique "chromatography" because he separated colored substances. We shall see, however, that the method is not so limited.

Tswett's work was ignored until the 1930's when a group of European chemists used his method to separate other colored plant extracts. From this point on, the developments came at an increasingly rapid pace and there is still no end in sight.

An analysis of what Tswett had done shows that he had utilized the difference in adsorbabilities of the substances in his mixtures on the surface of the chalk. At first, all of the components of the mixture were adsorbed on the chalk at the very top of the column. As the solvent passed through the column, the least strongly adsorbed component moved down the column most rapidly. The other components followed in the order of the adsorbabilities. Good separations were achieved when there were sufficient differences in the adsorbabilities of the various pigments.

A. J. P. Martin in England developed the idea of substituting for the solid adsorbent (used in Tswett's work) a solid coated with a liquid insoluble in the solvent used. This changed the physical basis for chromatography from differential adsorption to differential partition between the insoluble, "immobile" liquid phase and the solvent. The latter is called partition chromatography as contrasted to adsorption chro-

matography. Martin went on to the ingenious use of a sheet of filter paper with its absorbed water for a chromatography "column". This method of paper partition chromatography proved to be of revolutionary importance for the analysis of microgram quantities of a number of types of compounds, especially amino acids and carbohydrates. So great has been the usefulness of this tool to studies in protein chemistry, biochemistry, photosynthesis, and physiology that Martin was awarded the Nobel Prize in Chemistry in 1951.

In his original paper on column partition chromatography, Martin mentioned the possibility of separating a mixture of gases by passing them through a partition column in a stream of a carrier gas. While he was occupied with the development of paper chromatography, other workers successfully used adsorption columns to separate some gaseous mixtures. However, when attempts were made to extend the range to higher boiling substances by using heated columns, it was found that the adsorption method failed to give good separations. The partition technique, however, proved to be efficient well above room temperature. In fact, the upper limits of the temperature range for this technique have not yet been defined. Successful separations have involved high-boiling materials such as methyl behenate, the methyl ester of the C22 fatty acid. Even with the current state of development, any material which can be distilled at 1 mm pressure can probably be chromatographed by this method.

Elements of a Gas Chromatographic Apparatus

There are basically three parts of a gas chromatograph. These are the sample introduction system, the column, and the detection and collection system.

The problem of introducing the sample varies according to whether the sample is liquid or gaseous at room temperature. In either case, it is desirable to inject the sample as quickly as possible. Obviously, if the sample is introduced very slowly, it will not be possible to separate compounds traveling through the column at only slightly different speeds. The readily apparent effect will be to broaden the chromatographic peaks as registered by the detection system. For gases, the usual technique is to place the sample in a bypass system and introduce it by rapid manipulation of stopcocks. For liquids, the sample is usually injected by means of a hypodermic syringe through a rubber serum cap into the flowing gas stream. The best way to insure rapid volatilization of the liquid is to utilize a flash heater.

Since the sample is in the gaseous state, it is not necessary to maintain the column in a vertical position. The columns are filled in a vertical position to insure uniform packing of the solid in the column and then usually coiled for compactness. In this way, it is possible to use columns 25 feet or longer, even though a constant temperature control is most commonly provided by an air bath which may be varied from below room temperature to over 200°C.

A most important variable in the operation of a gas chromatograph is the choice of column packing. As stated previously, the packing consists of an inert solid on which is suspended a nonvolatile liquid. Some variations in performance can be obtained by choice of solid. Recent developments indicate that a crushed firebrick, probably because of its porous structure and optimum particle size, provides a better medium than the fine powders previously used.

The most startling changes in performance can be obtained by varying the nature of the nonvolatile liquid. In the gas partition techniques, we are dealing with two different effects which govern the rate of movement of compounds through the column. The first, the volatility of each component, tends to move components through the column in order of decreasing volatility. This effect operates analogously to a distillation. In addition, there is an associative or solution effect. This tends to slow down the passage of any compound which associates highly with the immobile liquid, or, to put it another way, is highly soluble in the immobile liquid. As a guide to predicting the nature of this effect, we may use the familiar rule of thumb, "like dissolves like". Thus, if one had failed to separate a mixture of an aromatic and an aliphatic compound on some nonassociating liquid such as silicone oil, the obvious next step would be to use an aromatic immobile liquid such as terphenyl or tricresyl phosphate. One would predict that the aromatic compound would associate much more strongly with

Since his association with Battelle, Charles Teitelbaum has carried on investigations relating to the separation and identification of natural products, essential oils, and combustion products. In connection with this research, he has been instrumental in the development, at the Institute, of a reference library of infrared spectra of aromatic chemicals and essential oil components. This collection of spectra has proved useful in identifying unknown specimens. Previously, he had studied the purification of antibiotics at the Antibiotics Division of Heyden Chemical Corporation. The author received his B.S. in chemistry from Brooklyn College and his M.S. in chemistry and Ph.D. in organic chemistry from Purdue University.

the immobile phase and thus be retained sufficiently longer to be separated. While there are limitations, based largely on volatility and heat stability, which govern the choice of compounds as immobile liquids, there is a large and constantly growing number to choose from. In order to increase the flexibility and efficiency of gas partition chromatography, there is a great need not only for more and better immobile liquids, but for a more systematic means of choosing the most suitable one for a particular problem.

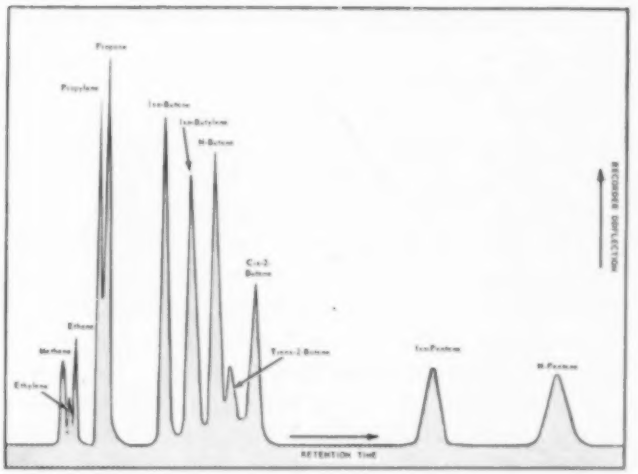
Detection and Collection System

One of the most serious limitations of liquid chromatography is the lack of a simple and generally useful method for detecting and measuring the appearance of the various fractions in the column effluent. In the case of colored fractions, visual observation is an obvious and effective means for detection and it can easily be made quantitative by spectrophotometric measurement. For colorless compounds, however, no generally useful physical measurement has been found which can analyze the effluent fractions for the low concentrations of desorbed compounds which are usually encountered.

The earliest work on gas partition chromatography involved the separation of the lower carboxylic acids, and a simple detection and measuring system based on an automatic titrimeter was used. The second technique used was based on an ingenious apparatus designed by Martin for detecting changes in the density of the gaseous effluent. Since most gases are denser than the commonly used carrier gas helium, an increase in gas density results as each fraction appears in the effluent. The magnitude of the increase is a quantitative measure of the amount of material in each fraction. However, this technique has not been widely used because of the difficulties in constructing the apparatus and certain operational shortcomings.

The most common detection method makes use of the fact that helium has a higher thermal conductivity than any other gas except hydrogen. The techniques of thermal conductivity measurement had been already worked out to a very high sensitivity and accuracy, and their adaptation to the needs of gas chromatography proved quite simple and effective. Two other properties that have been used for sample measurement are surface potential of solids and ionization under the influence of X-rays.

The thermal conductivity meter is a two-cell type. The helium passes through the reference cell, then through the column and finally through the measuring cell. The two cells are arms of a Wheatstone bridge so that a quantitative record of the thermal conductivity



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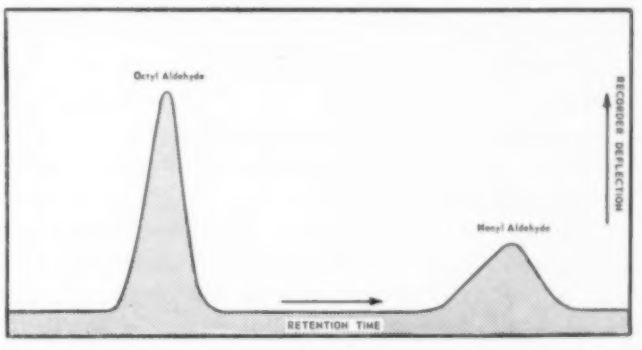

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2. *Typical gas chromatograms showing (a) a gas partition chromatogram of a mixture of low-boiling hydrocarbons and (b) a gas partition chromatogram of a mixture of octyl and nonyl aldehydes.*

is obtained by use of an electronic recorder.

Typical recordings are shown in Figure 2. Each peak corresponds to a different fraction of the starting materials and the quantitative or identifying feature is its retention time. In favorable cases and with proper calibration with known compounds, the retention time serves to identify the fraction. In many cases, however, identification must be done or at least confirmed by isolation of the fraction and subsequent measurement of other properties. The amount of each fraction is measured by the area under each peak. This can be estimated by a planimeter, or in some cases, by multiplying the height of the peak by the width at the half-peak height. In some commercially available machines, an automatic integrator records the area under each peak by a series of "pips" on the recording.

Sample collection can be accomplished by condensing each fraction in a cold trap or absorbing it in a volatile solvent. If larger samples are to be collected, it may be advisable to split the effluent stream and pass most of it directly into a trap while passing the smaller part through the thermal conductivity cell.

Advantages of Gas Chromatography

In speaking of the efficiency of gas chromatography for separating mixtures, comparison is usually made to distillation rather than to liquid chromatography. The reason is clear. Gas chromatography handles materials in the same physical state as does distillation and, in general, depends on the same differences in properties (i.e. vapor pressures) to effect separations. On the other hand, liquid chromatography, has had its greatest successes with nonvolatile substances and utilizes other differences in properties.

In comparison with distillation, gas chromatography offers a number of advantages. It is possible to separate mixtures of compounds whose boiling points are very close. Using the usual distillation concept of "theoretical plates" to express separation efficiency, gas chromatography routinely gives separations equivalent to 1000-2000 plates. On the other hand, extreme care is required to obtain more than 20 theoretical plates from distillation, particularly when operating under vacuum. The efficiency of distillation columns seldom exceeds 150 plates.

The ease of operation of a gas chromatograph is striking. It can be operated by almost anyone. The time required may range anywhere from ten minutes to two hours. Actually the analyst need only insert the sample then come back when it is done in the case of routine work. These features contrast with the trained supervision and prolonged times required for efficient distillations. In addition, a recording of each analysis is obtained without any additional manipulation.

In terms of sample sizes, gas chromatography can easily handle quantities far smaller than is possible even with "micro" distillations. The upper limit of sample sizes that can be conveniently handled by gas chromatography has not been reached; up to now, however, this technique has not been used to prepare large quantities of material. On the other hand, distillations in petroleum refineries routinely process tens of thousands of gallons.

Chromatography is also useful in separating azeotropes. Such constant-boiling mixtures often cannot be separated by distillation. However, neither azeotrope formation nor any analogous phenomenon has ever been observed to affect gas chromatography.

Another advantage of gas chromatography is that data obtained directly from a gas chromatogram may lead to determination of important physical properties of the substances involved. Thus, one can use the techniques to determine vapor pressures, heats of vaporization, and heats of solution. In the case of an homologous series of compounds, there is a straight-line relationship between the logarithm of the retention volume and the number of carbon atoms. This permits the determination of molecular weights from chromatographic data. It is also possible to tell something about the structure of a compound from its elution times with a variety of immobile liquids.

Applications of Gas Chromatography

Generally speaking, there are two ways one can utilize a gas chromatograph. It can be used as a direct analytical tool in which the thermal-conductivity record is used as a qualitative and quantitative analysis of the unknown. On the other hand, one may use the device as a tool for the isolation of pure compounds. In the latter case, the thermal conductivity record serves largely as a guide to the operation of the sample-collection system.

Up to the present time, the major use has been for the qualitative and quantitative analysis of light hydrocarbons. Typical analyses are shown in Figure 2. The speed, simplicity, and accuracy of this method are apparent and make it preferable to low-temperature distillation, infrared spectroscopy, mass spectroscopy or any other technique now available for production control and analysis of the more volatile hydrocarbons. Chemists have also analyzed alcohols, aldehydes, halogenated compounds, ether, esters, amines, acids, and fixed gases. The potentialities of this method make it obvious that the list of types of compounds amenable to analysis will continue to grow. There is no reason, for instance, why it should not be possible to apply the technique to volatile inorganic compounds.

The new tool has countless possible uses in the chemical and allied fields. For example, its use is feasible in such diverse fields as insecticides, essential oils and flavoring materials, other natural products, pharmaceuticals, solvents, combustion products, toilet goods, lubricants, refrigerants, coal tar, air pollution problems, and sundry synthetic chemicals. In fact, it has even been reported that nonvolatile materials such as plastics can be characterized by chromatography of their gaseous pyrolysis products. The only limitations on the materials to be handled are that they have a slight degree of volatility and have sufficient heat stability at the column temperatures required.

It is clear that the tremendous interest that gas chromatography has aroused is completely justified by the outstanding performance and exciting possibilities of this tool. When it is considered that the method is only a very few years old and that many further refinements can be expected, we can anticipate that its development will be considered as one of the significant technical accomplishments of this decade.

NOTES from BATTELLE

* RADIATION-EFFECTS STUDY

What effect does nuclear radiation have on the fuel material to be used in nuclear power reactors? This is one of many questions facing engineers who are designing reactors.

A description of an experimental program for determining radiation effects was presented last month by G .D. Calkins, who is in charge of Battelle's radioisotopes and radiation research, at a meeting jointly sponsored by the Atomic Industrial Forum and the American Society for Testing Materials. Coauthors of this paper, "A Radiation-Effects Program", were J. E. Whitney, E. M. Chandler, and J. E. Gates.

The authors estimate that a program of small-specimen radiation-effects research, which is one of the early stages of nuclear power reactor development research, might cost from ten to sixty thousand dollars for each batch of specimens irradiated, and run from eight to thirty months in length. The specimens are pieces of metal about one inch long containing uranium-235, the nuclear fuel. From one to six of them make up the batch that is loaded into a capsule for irradiation in a nuclear reactor. The need for remote handling procedures for the highly radioactive specimens after irradiation creates one of the major costs of this research. Much of this experimentation can be conducted only in "hot cells", which provide adequate shielding from large amounts of radiation.

Among the important properties of nuclear fuel that are affected by radiation are: dimensions, strength, hardness, ductility, corrosion resistance, conductivity, and ability to retain radioactive products formed during the fissioning of nuclear fuel. Measurements to determine the changes in these properties are made in inspections before and after irradiation. In addition, measurements of some variables, such as temperature, are made during irradiation.

The design and loading of the capsules, which are made of stainless steel, aluminum, or zirconium, is one of the major parts of the program because of the important role the capsule has in controlling variables, particularly temperature, that influence radiation effects. Very roughly, the total cost of a small specimen research program is divided approximately in thirds among the capsule design, loading and specimen inspection prior to irradiation; the irradiation itself; and the post-irradiation inspections and experiments.

The authors point out that experiments such as these are an integral part of research to create more efficient reactors. They note that at present only about one per cent of the atoms in a fuel element in a reactor are "burned up" in nuclear fission. If the capacity of a nuclear fuel material to withstand radiation can be increased, technologists can raise the fraction of the fuel atoms burned up before reprocessing to remove radioactive wastes becomes necessary. The economic efficiency of power reactors improves markedly as the attainable burn-up increases. After technologists have learned to fabricate potential fuel materials, radiation-effects research is the next important step in their evaluation.

After the small-specimen experiments described above establish the stability of a particular fuel material, proof testing with small prototype fuel elements or a mockup of a full-scale assembly are needed to demonstrate the over-all worth of the experimental fuel material.

* POROUS ALLOY ELECTROPLATING

Porous electroplates of an alloy of nickel and cadmium have been produced by electrochemists at Battelle. In previous research, Battelle technologists determined how to produce porous electroplates of such single metals as nickel, zinc, and copper. The present study, results of which were presented in a paper at the 43rd annual convention of the American Electroplaters' Society in Washington, describes the conditions needed to produce a porous electroplate of an alloy of nickel and cadmium.

The conditions leading to such a porous alloy are fairly rigid, according to L. D. McGraw, J. P. Spenard, and C. L. Faust, authors of the paper. Aqueous solutions of sulfate and chloride salts of nickel and cadmium form the electrolytic bath, which will only produce porous plates in the acidity range of pH 5-6. Best results were obtained when the bath was operated at 135 F with a current density of 150 amp/sq ft. Little control could be exercised over plate composition in excess of five per cent cadmium at the high pH of 5-6 required for plating a porous alloy from the sulfate-chloride bath.

The Battelle technologists found that when porosity

was not a requirement, the sulfate-chloride bath could be operated to produce a fair range in the proportion of cadmium to nickel, while a wide range of cadmium to nickel could be obtained using a fluoborate bath. Such ranges in composition were obtained by operating the baths below pH 5-6.

Plate thicknesses up to 0.015 inch, considerably thicker than decorative electroplates, were produced in this experimentation, which was conducted for the U. S. Army, Signal Corps Engineering Laboratories.

* SOFT X-RAY STERILIZATION

Low-voltage, or "soft", X-rays may prove to be the radiation of choice for a number of pharmaceutical sterilization operations. When surfaces or thin layers of materials are to be treated, low-voltage X-rays may provide a commercially economic sterilization method.

These statements were addressed to scientists at the annual meeting of The Society for Industrial Microbiology, which met under the auspices of the American Institute of Biological Sciences at the University of Connecticut. They were made in the paper, "The Use of Soft X-Rays in the Sterilization of Pharmaceuticals", by Dr. F. E. Porter of Battelle.

Among the products that have been treated with soft X-Rays in the course of experiments at Battelle are penicillin, Vitamin B_{12}, and riboflavin. Each was sterilized without loss of potency.

Compared with diagnostic X-rays, soft X-rays are characterized by lower penetrating power, higher flux density (output of radiation energy per unit of area) and longer wave length. Commercial X-ray units are generally built to operate at voltages ranging from 250,000 volts to one million volts. Soft X-rays, by contrast, are low-voltage radiation produced by units operating in the range of 2500 to 250,000 volts.

Battelle experimentation with low-voltage radiation on pharmaceuticals, foods, and other materials has been conducted with a unit composed of conventional transformers and a prototype X-ray tube with a novel beryllium window. The tube, built by Machlett Laboratories, Springdale, Connecticut, operates at 60 kilovolt peak and 200 milliamperes. It is designed for continuous operation on existing production lines and requires only one nontechnical operator.

The beryllium window in the experimental tube transmits the longer, soft X-ray wave lengths. Soft X-rays are absorbed efficiently, states Dr. Porter; five millimeters of water absorb 90 per cent of the energy of the beam. Thus, the shielding for a soft X-ray unit can be provided relatively economically.

* Chloral hydrate, which has been used in pharmaceuticals, and is now used in tonnage amounts in a variety of organic compounds including DDT, has been the subject of study at Battelle's Geneva laboratory. Chemists there investigated the process by which anhydrous chloral adds one molecule of water to form a stable crystalline hydrate. They found that, during hydration, an intermediate is formed containing one molecule of water for two molecules of chloral.

Like the hydrate, this intermediate is a solid crystalline product. The chemists, on the basis of infrared analysis, have suggested the possible structure of the intermediate.

* A paper by Battelle chemists Clara Smith and E. R. Mueller has been selected to receive this year's Carbide and Carbon Chemicals Award. The Award is given each year for the best paper presented before the Division of Paint, Plastics, and Printing Ink Chemistry of the American Chemical Society. Mrs. Smith and Mueller received the Award at the Fall Meeting of the ACS in Atlantic City. The paper, "The Effect of Driers on Composition and Physical Characteristics of Linseed Oil and Varnish Films—A Chemical and Infrared Study", was presented at the ACS meeting in September, last year.

* Joel W. Chastain, Jr. has been appointed chief of Battelle's newly established reactor physics division. Since his association with the Institute, he has aided in the design of its research reactor and critical assembly (reactor development) laboratory. He has also shared responsibilities in the establishment and administration of those facilities of which his new division is now in charge. Chastain has carried on investigations in the fields of reactor physics, reactor-core design, heat transfer, and thermal stresses.

He came to Battelle from the Case Institute of Technology where he worked with the betatron for a number of years. He received his M.S. in physics from Case after previously graduating from Kent State University with a B.S. in physics.

* A bibliography of published materials relating to the corrosion of cobalt and cobalt alloys is now available from the Cobalt Information Center at Battelle. The bibliography contains entries from European as well as American publications. Many of the items are annotated. The work was prepared by F. R. Morral.